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Adsorption of acid dyes onto bentonite modified with polycations: Kinetics study and process design to minimize the contact time

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ABSTRACT

The adsorption kinetics of two acid dyes, Acid Scarlet GR and Acid Dark Blue 2G, onto a bentonite modified with poly-epichlorohydrin-dimethylamine (EPI-DMA) was studied. The pseudo second-order model showed a high degree of correlation with the experimental data for the whole adsorption process, whereas the intraparticle diffusion model presented two steps with two different diffusion rate constants indicating that the intraparticle diffusion may be involved in the adsorption process during the first 15 min. A two-stage batch adsorber was designed based on the second-order kinetics and was optimized to minimize the total contact time.

1. Introduction

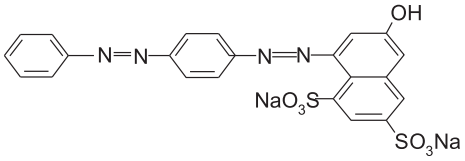
Well-designed adsorption processes presented high efficiency resulting in a high-quality effluent after treatment at lower cost (Ho and McKay, 1999a). Low-cost adsorbents would keep the low cost. To minimize the contact time for a fixed degree of pollutant would increase the amounts of wastewater being processed each day. Consequently, the size of the required plant facilities could be reduced and the cost decreased (Özacar, 2006; Özacar and Şengil, 2006). Polycation-modified bentonite was proved to be of high efficiency for dye removal (Churchman, 2002; Kang et al., 2009; Özcan et al., 2007; Yue et al., 2007a, 2007b). Although organo-bentonites could have similar properties, at strong acidic conditions, organic species can be leached and enter the water system as pollutant while polycations have a much stronger affinity to bentonite and are not easily desorbed.

A well-designed adsorption process for the dye-polymer/bentonite system is necessary for the application in actual dye-wastewater treatment, especially for the purpose of reducing operating cost. However, there were only a few reports of such studies. Hence, the purpose of this study was to focus on the adsorption kinetics and process design of dyes onto polycation/bentonite. The acid dyes, Acid Scarlet GR (AS-GR) and Acid Dark Blue 2G (ADB-2G), were chosen as the model system due to their high water solubility and wide application in dyeing of nylon, wool, silk, etc. The polycation poly-epichlorohydrin-dimethylamine (EPI-DMA) which was proved to be non-toxic (Choi et al., 2001; Joo et al., 2003) was used to modify the bentonite (EPI-DMA/bentonite). EPI-DMA/bentonite could absorb both anionic and cationic compounds, which could be an advantage over individual bentonite or EPI-DMA. Based on the kinetics studies, a two-stage batch adsorber was designed by Ho and McKay (1998, 1999b) and used for the acid dye–EPI-DMA/bentonite system. A design analysis was used to predict the minimum contact time for removing a given degree of the acid dye at a given volume of wastewater effluents with a fixed initial concentration using a specified amount of the adsorbent.

2. Materials and methods

2.1. Materials

Acid Scarlet GR (AS-GR) and Acid Dark Blue 2G (ADB-2G) were supplied by Binzhou Dye Printing Co. Ltd. (Shandong, China). The structural formula of AS-GR is



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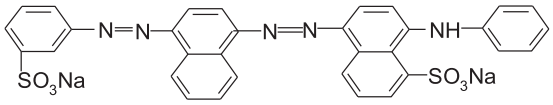
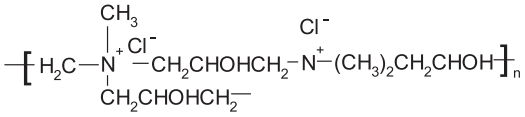
and that of ADB-2G is



The polycation poly-epichlorohydrin-dimethylamine (EPI-DMA) was produced by Binzhou Chemical Co. Ltd. (Shandong, China). Its structural formula is



The raw bentonite was obtained from the city of Weifang in Shandong, China and was used without any purification. The cation exchange capacity (CEC) was 0.70 meq/g.

2.2. Preparation and characterization of EPI-DMA/bentonite

To prepare the polymer/bentonite, 100 mL of 5% of EPI-DMA solution was added to a dispersion containing 20 g bentonite (Yue et al., 2007a). The dispersion was stirred at 70 °C for 2 h. The polymer/bentonite was separated by filtration, washed, and dried at 110 °C (EPI-DMA/bentonite).

2.3. Adsorption experiments

A definite amount W (0.1 g) of EPI-DMA/bentonite was dispersed in 100 mL of the dye solution of known concentration C_0. The dispersions were shaken on a horizontal shaker. The dye concentration was 50 mg/L, except those in which the effect of concentration was investigated. The solution initial pH was 7.5 for AS-GR and 7.9 for ADB-2G, except when the effect of pH was considered. The temperature of the system was kept constant at 303 K, except when the effect of temperature on the adsorption was examined. The dye concentration C_t in the clear supernatant at different time intervals was determined by spectrophotometry. The standard deviation of the concentration measurements was ±5.0%. The amount of adsorbed dye Q_t (mg/g) was calculated from the concentration differences.

2.4. Adsorption kinetics

The adsorption data were fitted by three models.

The linear form of the pseudo first-order kinetic equation is

$$\ln\left(Q_{e,1}-Q_t\right) = \ln Q_{e,1} - k_1 t \tag{1}$$

where k_1 is the equilibrium rate constant of pseudo first-order adsorption (1/min), $Q_{e,1}$ and Q_t are the amounts of dyes adsorbed at equilibrium and at time t (mg/g).

The pseudo second-order equation describes the process over the whole period of adsorption. The linear form is

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{e,2}^2} + \frac{t}{Q_{e,2}} \tag{2}$$

where k_2 is the equilibrium rate constant (g/mg min) and $Q_{e,2}$ is the equilibrium adsorption amount (mg/g). The initial adsorption rate was derived from h ($h = k_2 Q_{e,2}^2$) [mg/(g min)] (Ho and McKay, 1999b).

The possibility of intraparticle diffusion during adsorption was examined by using the intraparticle diffusion model

$$Q_t = k_{\text{int}} t^{0.5} + C \tag{3}$$

where k_{int} is the intraparticle diffusion rate constant [mg/(g min$^{0.5}$)], and C is a constant proportional to the boundary layer thickness.

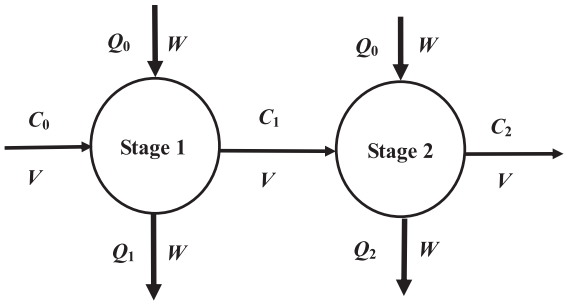


Fig. 1. Two-stage batch adsorption process for dye removal.

2.5. Adsorption process design

The adsorption kinetic equations could be used to predict the design of batch adsorption processes, which in turn gave an insight into the optimized contact time in wastewater treatment. Thus, a two-stage batch adsorption system (Ho and McKay, 1998, 1999a; Özacar, 2006; Özacar and Şengil, 2006) was designed (Fig. 1).

The inflow containing the solution with volume V and an initial dye concentration C_0 entered the first batch adsorber. After adsorption and separation, the solution with the dye concentration C_1 was transferred to the second adsorber. The dye concentration of the effluent from the second adsorber became C_2. The amount of added adsorbent at each stage was W and the initial dye concentration was Q_0. The dye adsorbed in each stage increased from Q_0 to Q_i ($i = 1, 2$). At time t, the dye adsorption at each stage, Q_i, became $Q_{t,i}$. When a fresh adsorbent was used, $Q_0 = 0$. The mass balance in each stage in the two-stage adsorption system could be expressed as

$$V(C_{i-1}-C_i) = W\left(Q_{t,i}-Q_0\right) = WQ_{t,i} \tag{4}$$

In the two-stage adsorption system, $Q_{t,i}$ could be well described by the pseudo second-order equation. Thus, the mass balance equation for each stage may be obtained by combining Eqs. (2) and (1) as follows:

$$C_{i-1}-C_i = \frac{WQ_{t,i}}{V} = \frac{WkQ_{e,i}^2 t_i}{V\left(1 + kQ_{e,i}t_i\right)} \tag{5}$$

The total amount of dye removal by the two-stage adsorption system was

$$\sum_{i=1}^{2}(C_{i-1}-C_i) = \sum_{i=1}^{2}\frac{WkQ_{e,i}^2 t_i}{V\left(1 + kQ_{e,i}t_i\right)} \tag{6}$$

The dye removal in each adsorption stage, R_i, was calculated as follows:

$$R_i = \frac{C_{i-1}-C_i}{C_0} = \frac{WkQ_{e,i}^2 t_i}{V\left(1 + kQ_{e,i}t_i\right)C_0} \tag{7}$$

Thus, the total dye adsorption was obtained by

$$\sum_{i=1}^{2} R_i = \sum_{i=1}^{2}\frac{Wk_2 Q_{e,i}^2 t_i}{V\left(1 + k_2 Q_{e,i}t_i\right)C_0} = \frac{W}{VC_0}\sum_{i=1}^{2}\frac{kQ_{e,i}^2 t_i}{1 + kQ_{e,i}t_i} \tag{8}$$

k and Q_e could be expressed as a function of the solution concentration entering each adsorber, C_{i-1} ($i = 1, 2$), as follows:

$$k = X_k C_{i-1}^{Y_k} \tag{9}$$